Hydrosilanes as Reducing Reagents of Copper Salts into Copper Metal Particles under Remarkably Mild Conditions

Masaki Takahashi, Jun Kamada,* Kenji Iwata, Kenichi Goto, Hiroshi Watanabe, and Shoji Tamai

Material Science Laboratory, Mitsui-Chemicals, Inc.,
580-32 Nagaura, Sodegaura 299-0265

Received February 8, 2007; E-mail: Jun.Kamada@mitsui-chem.co.jp

Copper nanoparticles were synthesized using hydrosilanes as a reducing agent. The reaction smoothly occurred under remarkably mild conditions, i.e., room temperature. This reaction depended on the counter anions of the copper salts and the structure of the hydrosilanes, and their role is discussed.

Organosilanes, especially polysilanes, are known to reduce noble metal salts and silver salts into the corresponding noble metal particles due to the high-HOMO-electron of the Si–Si bonds.[1] However, these compounds cannot reduce transition-metal ions with low standard redox potentials. Hydrosilanes are known to reduce organic compounds, such as the hydrosilylation of organic compounds having unsaturated bonds using a noble metal catalyst,[2] but using these compounds to reduce metal salts is still undeveloped. Anderson has reported the only example, wherein a copper (Cu) salt is reduced to metallic Cu using a hydrosilane. However, they obtain only a trace amount of Cu metal, and the analysis is ambiguous.[3]

Recently, metal particles, especially nano-sized particles, have been frequently highlighted for new applications due to their unique properties. Other metal particles have also been used in industries, for example, the manufacturing of conductive pastes for use as materials in conducting lines of a circuit or for new magnetic materials. Cu nanoparticles are particularly useful because of their catalytic, optical, and conducting properties and low cost. A number of methods have been developed for the preparation of Cu nanoparticles, such as thermal decomposition,[4] the sonochemical method,[5] electrodeposition,[6] chemical reductions,[7–10] etc.

In this study, the reactivity of hydrosilanes as reducing agents for Cu salts was investigated, and the preparation of Cu nanoparticles was achieved using some hydrosilanes under quite mild, safe, and facile conditions.

First, the reduction of some Cu^I salts with phenylsilane ($PhSiH_3$) were examined. The procedure for this type of reaction involved dispersing Cu salts at 500 mM in acetonitrile in the presence of the proper mole ratio of $PhSiH_3$ under a nitrogen atmosphere at room temperature. When $Cu(OCOCH_3)$ or CuCl were used as the Cu salts, a black precipitate appeared within 30 min. In that case, the solution after the solvent was removed by flowing nitrogen, and a residual black powder was obtained after decantation and drying under vacuum. Analysis of the black powder was carried out using the XRD technique (Fig. 1). The results, summarized in Table 1, suggest the selectivity is controlled by the counter anions of the Cu salts. $Cu(OCOCH_3)$ was completely reduced to Cu metal (Entry 1), and CuCl was mainly reduced to Cu metal (Entry 2). Copper salts seem to be easily reduced when Pauling's electronegativity of the charged atom of the counter anion of Cu^I salt is high. For the reaction of $Cu(OCOCH_3)$ and $PhSiH_3$, the product was analyzed by elemental analysis, and the result showed that 93% Cu was obtained.

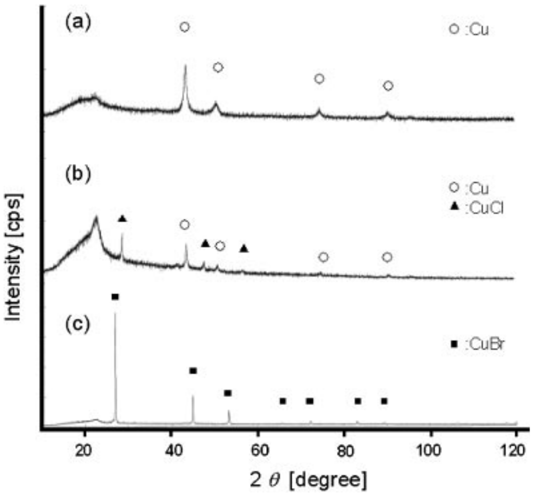

Fig. 1. X-ray diffraction patterns of products from the reactions of $PhSiH_3$ with Cu^I salts; (a) the Cu salt is $Cu(OCOCH_3)$; (b) CuCl; (c) CuBr.

Table 1. Reaction of Cu^I Salts with $PhSiH_3$ in Acetonitrile

Entry	Copper salt (A)	Hydrosilane (B)	Mol ratio (B)/(A)	Product[a)]
1	$Cu(OCOCH_3)$	$PhSiH_3$	2	Cu
2	CuCl	$PhSiH_3$	2	Cu, CuCl
3	CuBr	$PhSiH_3$	2	CuBr

a) Identified by XRD.

Table 2. Reaction of Cu^I Acetate with $PhSiH_3$ in Various Organic Solvents

Entry	Copper salts (A)	Hydrosilane (B)	Solvent	Mol ratio (B)/(A)	Product[a)]
1	$Cu(OCOCH_3)$	$PhSiH_3$	Acetonitrile	2	Cu
4	$Cu(OCOCH_3)$	$PhSiH_3$	THF	2	Cu
5	$Cu(OCOCH_3)$	$PhSiH_3$	Hexane	2	Cu
6	$Cu(OCOCH_3)$	$PhSiH_3$	Ethanol	2	Cu
7	$Cu(OCOCH_3)$	$PhSiH_3$	Methanol	2	$Cu(OCOCH_3)$, CuO

a) Identified by XRD.

The solvent dependence of the reaction using $PhSiH_3$ and $Cu(OCOCH_3)$ is shown in Table 2. This result shows that $Cu(OCOCH_3)$ can be reduced in most solvents, meaning that the solvent dependence of this reaction is small. Solid $Cu(OCOCH_3)$ was also reduced to Cu (Entries 1 and

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Table 3. Reaction of Cu^{II} Salts with $PhSiH_3$ in Acetonitrile

Entry	Copper salt (A)	Hydrosilane (B)	Mol ratio (B)/(A)	Product[a]
8	$Cu(OCOCH_3)_2$	$PhSiH_3$	4	Cu
9	$CuCl_2$	$PhSiH_3$	4	CuCl
10	$CuBr_2$	$PhSiH_3$	4	CuBr
11	$CuSO_4$	$PhSiH_3$	4	$CuSO_4$

a) Identified by XRD.

Table 4. Reaction of Cu Salts with Hydrosilanes in Acetonitrile

Entry	Copper salt (A)	Hydrosilane (B)	Mol ratio (B)/(A)	Product[a]
1	$Cu(OCOCH_3)$	$PhSiH_3$	2	Cu
12	$Cu(OCOCH_3)$	Ph_2SiH_2	3	Cu
13	$Cu(OCOCH_3)$	Ph_3SiH	6	Cu, Cu_2O
14	$Cu(OCOCH_3)$	$(C_2H_5)_2SiH_2$	3	Cu, Cu_2O
15	$Cu(OCOCH_3)$	$(C_2H_5)_3SiH$	6	Cu, Cu_2O
16	$Cu(OCOCH_3)$	$(CH_3O)_2MeSiH$	6	Cu, Cu_2O
2	CuCl	$PhSiH_3$	2	Cu, CuCl
17	CuCl	Ph_2SiH_2	3	Cu, CuCl
18	CuCl	Ph_3SiH	6	CuCl
19	CuCl	$(C_2H_5)_2SiH_2$	3	CuCl
20	CuCl	$(C_2H_5)_3SiH$	6	CuCl
21	CuCl	$(CH_3O)_2MeSiH$	6	CuCl
8	$Cu(OCOCH_3)_2$	$PhSiH_3$	4	Cu
22	$Cu(OCOCH_3)_2$	Ph_2SiH_2	6	Cu
23	$Cu(OCOCH_3)_2$	Ph_3SiH	12	Cu (trace)
24	$Cu(OCOCH_3)_2$	$(C_2H_5)_2SiH_2$	6	Cu
25	$Cu(OCOCH_3)_2$	$(C_2H_5)_3SiH$	12	N.D.
26	$Cu(OCOCH_3)_2$	$(CH_3O)_2MeSiH$	12	Cu, Cu_2O

a) Identified by XRD.

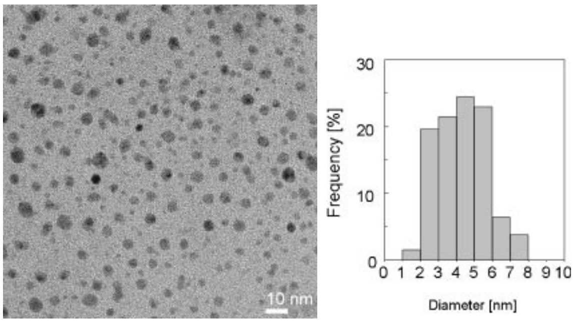


Fig. 2. TEM image and size distribution of Cu nanoparticles at $[Cu(OCOCH_3)] = 20\,mM$ and $[PhSiH_3] = 40\,mM$.

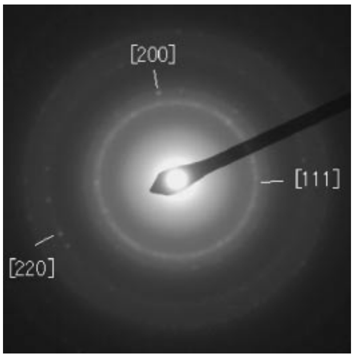


Fig. 3. Electron diffraction patterns of Cu nanoparticles at $[Cu(OCOCH_3)] = 20\,mM$ and $[PhSiH_3] = 40\,mM$.

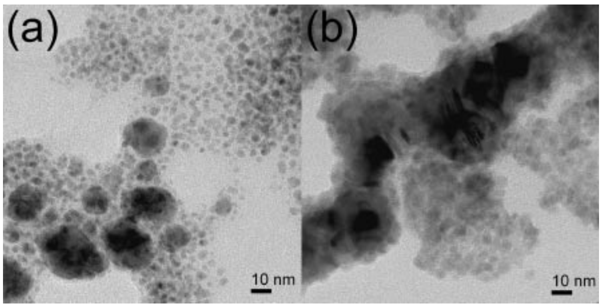


Fig. 4. Typical TEM images of Cu particles at $[Cu(OCOCH_3)] = 20\,mM$; (a) $[Ph_2SiH_2] = 60\,mM$; (b) $[(C_2H_5)_2SiH_2] = 60\,mM$.

4–6). In the case of methanol, it seems to react with $PhSiH_3$ (Entry 7).

The reduction of Cu^{II} salts was attempted using $PhSiH_3$ (Table 3) Though the Cu^{II} ion has a very low standard redox potential, copper(II) acetate was also reduced to Cu metal. Other Cu^{II} salts were reduced to the corresponding Cu^{I} salts. When using Cu^{II} salts, a similar selectivity of the salt anion to the Cu^{I} salts was observed.

The structure dependence of the hydrosilanes in this reaction was examined, and the results are summarized in Table 4. These results seem to show that the $Cu(OCOCH_3)$ is better reduced when a phenyl group is present in the hydrosilane (Entries 1, 12, 2, 17, 8, and 22) than when an alkyl group or alkoxy group is present. However, for the triphenylsilane, steric hindrance or an electric effect of the phenyl groups seems to lower the reductivity of the hydrosilane (Entries 13, 18, and 23).

Identification of the products from this reaction from $PhSiH_3$ was somewhat difficult because of the complexity of the products; thus, we analyzed the product from triethylsilane. The reaction solution obtained from $Cu(OCOCH_3)$ and triethylsilane was analyzed by GC-MS. The reaction solution had the smell of acetic acid. GC-MS peaks assignable to acetoxyltriethylsilane, triethylsilanol, and 1,1,1,3,3,3-hexaethyldisiloxane were observed. The latter two products are thought to form from the hydrolysis of acetoxytriethylsilane and the dehydrating dimerization of the formed silanol.

Transmission electron micrograph of the resulting precipitate, obtained using 20 mM $Cu(OCOCH_3)$ and 40 mM $PhSiH_3$ in ethanol, showed highly dispersed 1–8 nm sized Cu particles (Fig. 2). The electron diffraction pattern for the resultant nanoparticles, as shown in Fig. 3, showed they are pure metallic Cu particles. $PhSiH_3$ seems to act as both a reducing agent and a capping agent. On the other hand, in the case of using other hydrosilanes, the Cu particles were partially or completely coherent. Typical TEM images are shown in Fig. 4.

The UV–vis spectrum obtained using 2 mM $Cu(OCOCH_3)$ and 4 mM $PhSiH_3$ in acetonitrile is shown in Fig. 5. The plasmon absorption band of Cu nanoparticles appeared at 590 nm, which is in good agreement with the reported values with absorption maxima from 570 to 590 nm.[10]

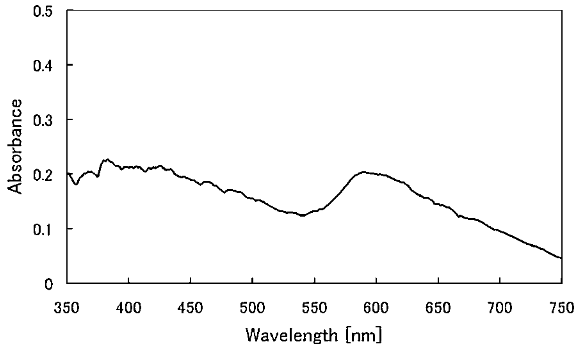
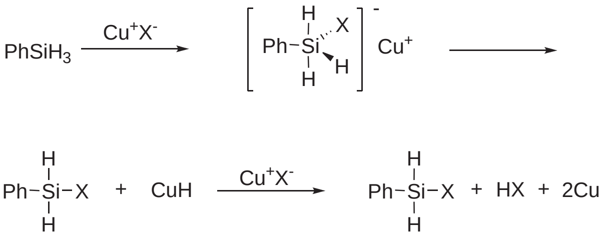


Fig. 5. UV–vis spectrum of the reaction solution obtained at [$Cu(OCOCH_3)$] = 2 mM, [$PhSiH_3$] = 4 mM.



Scheme 1.

The most plausible mechanism of the reducing reaction using $PhSiH_3$ is considered as shown in Scheme 1. Scheme 1 is based on the fact that hyper-coordinated hydrosilanes exhibit a higher reducing ability than the four-coordinate hydrosilanes to organic carbonyl or carboxyl compounds.[11] In this mechanism, the acetate anion of $Cu(OCOCH_3)$ coordinates to the silicon atom of the hydrosilane to form a five-coordinate hydrosilane, which is expected to have a stronger reducing ability than the starting the four-coordinate hydrosilane species. The five-coordinate hydrosilane reacts with the Cu cation to form copper hydride (CuH). CuH then reacts with another $Cu(OCOCH_3)$ to form Cu metal and acetic acid. Based on a strong anion dependence, the mechanism of Scheme 1 seems to be operative, because the rate determining step of Scheme 1 is considered to be the formation of the five-coordinate silicon species, in which the anion effect would be quite high. The phenyl group of the hydrosilane seems to stabilize the five-coordinate hydrosilane anion by electron delocalization.

In conclusion, some of the Cu salts were reduced to metallic Cu nanoparticles using hydrosilanes in solvents under very mild conditions. As a Cu salt, the acetates were the most easily reduced. $PhSiH_3$ promoted the formation of Cu nanoparticles with a lower degree of size dispersity.

Experimental

All reagents were commercially available and used without further purification. All of the solvents used in this reaction were commercially available anhydrous solvents and used without further purification.

A typical procedure for the preparation of the Cu particles is as follows. The Cu salt was dispersed in a solvent at 20–500 mM under a nitrogen atmosphere. To this dispersion, the proper molar ratio amount of the hydrosilane was added. The mixture was then stirred for 30 min.

The sample for the elemental analysis was prepared by decantation and washing of the reacted mixture with THF. The weight of the product obtained after the reaction using $Cu(OCOCH_3)$ (1.01 g, 8.24 mmol) of and phenylsilane (1.82 g, 16.8 mmol) was 0.54 g. Elemental analysis of this sample showed 89% Cu, 5.7% silicon and carbon, 5.5% oxygen, with 93% Cu being obtained. XRD patterns were measured using an X-ray diffractometer (Rigaku, model Rotaflex, Tokyo) employing Cu Kα radiation. The XRD patterns were recorded at 2θ from 10° to 120° using a fixed time method with a sampling step of 0.01°. The identification of the products was carried out by comparing the peaks to authentic samples. The elemental analysis was carried out using a CHN analyzer (Perkin-Elmer, 2400II, MA) and ICP-AES analyzer (Seiko Instruments, model VISTA-PRO, Tokyo). The copper particles were observed by TEM using a JEOL model JEM-2200FS at 200 kV. The samples for the TEM analysis were prepared by diluting a dispersed Cu solution with water, placing a drop of the solution on a collodion-covered copper grid, and then, drying it in air at room temperature. UV–vis absorption spectrum of the reaction solution was measured using a spectrometer (Shimadzu, model MultiSpec-1500, Kyoto).

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